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Understanding the dynamics of phosphorus sorption in acidic soil amended with cocoa pod husk biochar

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Abstract

Cocoa pod husks (CPH) generated from cocoa gardens, after separation of beans from cocoa pods, were converted to biochar through pyrolysis. Though biochar itself is a source of many vital nutrients, it has got high capacity for nutrient sorption, much more than natural organic matter, by some estimates even 10 to 100 times. In soils, phosphorus exists mostly in organic and inorganic forms and many times become a limiting nutrient in acidic and alkaline soils because of adsorption, precipitation and complexation. Hence, better understanding of phosphorus sorption dynamics in soil is a key to know the bioavailability of P in a soil. In this study, an attempt was made to examine the P sorption vis-à-vis desorption properties when cocoa pod husk biochar is applied in an acidic soil with three different levels of phosphorus availability. The biochar was applied @ 0, 5, 10, 20 and 40 g kg^{-1} to the acidic field soils which received inorganic fertilizer with and without organics and also unfertilized soils. Phosphorus retention and release was studied by fitting the equilibrium solution and sorbed concentrations of P by adsorption isotherms. The results showed that in all the soil biochar incubation treatments, increased biochar addition led to an increase in the soil available P and the P activation coefficient. In the sorption-desorption study, it was found that phosphorus sorption increased with increasing rates of biochar application. The addition of biochar at 20 g kg^{-1} and 40 g kg^{-1} increased the equilibrium solution P concentration and increased available P as compared to lower doses of biochar. Also, fertilized soils sorbed more phosphorus (323.25 – 995.27 mg kg^{-1}) than un-fertilized soils (347.25 - 805.47 mg kg^{-1}) @ 0–40 g kg^{-1} biochar. All the treatments fitted satisfactorily with Langmuir equation (r^2 = 0.96–0.99, P = 0.01) and Freundlich equation (r^2 = 0.87–0.99, P = 0.01). In this paper, we explain the phosphorus adsorption features using Langmuir equation as the main isotherm. The conclusion drawn from this study was that the addition of CPH biochar could alter the P availability, which is directly related to the phosphorus sorption dynamics of the soil.

Keywords : *Phosphorus, sorption, cocoa pod husk biochar, acidic soil*

Introduction

Biochar, the black carbon material generated from bio-wastes, by a process known as pyrolysis, is widely accepted as a soil amendment mainly because of its chemical and physical properties and large surface area. Biochar is reported as a source of plant nutrients and carbon and hence known to improve soil properties like nutrient availability (Glaser *et al*., 2002; Sohi *et al*., 2010), water holding capacity (Masiello *et al.*, 2015; Liu *et al*., 2017) and sequester carbon for long time (Woolf *et al*., 2010). The properties of biochar vary with the feed stock materials and the range of temperature in which it is produced. There are reports that the pyrolysis temperature has a positive correlation with the pH and nutrients like potassium, phosphorus, etc. but has a negative correlation with nitrogen (Hossain *et al*., 2020). Addition of biochar in soil helps to improve the nitrogen and phosphorus in soil by reducing the leaching losses. Biochar can also alter the content of other plant nutrients in soil depending on the type of feedstock and rate of application. Also, there are reports that biochar can modify the biological properties of soil by improving the microbial biomass and enzyme production. In these ways, biochar serves as a superior natural source of nutrient pool and a good soil amendment.

Soil application of biochar has been reported to improve the bioavailability of phosphorus and hence, plant growth (DeLuca *et al*.,

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2009). The amount of phosphorus supply from biochar mainly depends on the type of feed stock and the content of phosphorus present in the feed stock. The temperature of the biochar preparation is reported to have less influence on the phosphorus bioavailability in soil (Gang Xu *et al*., 2014). It was reported that in sandy or loamy soils, the addition of biochar significantly improved the available phosphorus (Tryon, 1948). Also, it was noted that application of biochar could reduce phosphorus availability temporarily and did not affect the phosphorus availability upon addition of more phosphorus (Sandeep *et al*., 2013). The alkaline nature of biochar play a very important role in altering the pH of the soil which in turn alter the complexing character of phosphorus with metal cations like Al^{3+}, Fe^{3+} and Ca^{2+}. The mechanism of sorption and desorption reactions play a great role in these complexation reactions. The sorbed phosphorus may slowly become available to plants by the process of desorption for long time, as it is locked in the soil-biochar matrix. Compared to desorption, the sorption is very important and considered strongly to form suitable management practices.

Cocoa (*Theobromae cacao* L.), a crop of humid tropics is an important plantation crop grown for its beans, widely used in the preparation of chocolates. After the removal of the beans, the cocoa pod husks are left in the field along with other cocoa plant debris and these acts as inoculum for many pod rot diseases. To obviate it, effective use of cocoa pod husks was made by converting them into biochar by the process of pyrolysis under oxygen-limiting conditions. In an earlier study, cocoa pod husks were found suitable for biochar conversion and found to have good amount of all plant available nutrients especially phosphorus and potassium (personal communication). Biochar, in general, can sorb the phosphorus present in the soil solution and prevent the loss of soil phosphorus by leaching. Hence, this study was carried out to understand the effect of cocoa pod husk biochar on phosphorus sorption –desorption behavior in an acidic loamy soil. The knowledge on interaction of cocoa pod husk biochar with soil can provide important inference on phosphorus availability in P-deficient soil and its management.

Materials and Methods

Characteristics of Soil and Biochar

The soil samples were collected from long term fertilizer-cum-manurial plots under coconut established at CPCRI, Kasaragod agricultural farm during 1972 (12º53' N latitude and 74º 97' E longitude with an altitude of 10.7 m above mean sea level). The climate of the area is classified as warm humid tropical with an average maximum temperature of 31.2°C and minimum temperature 23.6ºC. The mean annual rain fall of the area is 3462 mm. Three different types of soil samples were collected from the coconut basins at 0-30 cm depth: unfertilized (did not receive any fertilizer), inorganic fertilizer alone (received 100% NPK) and inorganic + organic fertilizers (received 100% NPK+ organic manures @50 kg green leaves per palm per year). The collected soil samples were air dried and passed through 2 mm mesh sieves. The soil samples were analyzed for pH, total N, available phosphorus, available potassium, exchangeable calcium and magnesium as per the procedures summarized by Jackson (1973). The determination of Walkley and Black carbon was performed with the wet digestion method (Walkley and Black, 1934). The micronutrients like iron, manganese, zinc and copper were extracted using DTPA and analysed in AAS as per the procedure outlined by Lindsay and Norvell (1978). The soil is classified as red loamy-sand containing on an average 86-88% sand. The chemical characteristics of the soils under study are presented in Table 1.

The cocoa pod husk was collected from the cocoa fields after separating out the cocoa beans. The cocoa pod husks which have no economic value were dried in sun and then converted to biochar using a kiln procured from ICAR-Central Institute of Agricultural Engineering, Bhopal, India. This cocoa pod husk (CPH) biochar produced was crushed manually and ground to pass through 2 mm mesh sieve for initial analysis and also to use for the incubation experiment. The CPH biochar was analysed for pH and EC, which were estimated in 1:10 solid to solution ratio after shaking for an hour in a reciprocating shaker and kept for half an hour and read in pH/EC meter (Lee *et al*., 2013). Organic carbon content of biochar was estimated by Walkley and Black method (1934). Total nitrogen was determined by wet digestion using concentrated sulfuric acid (Jackson 1973). The total phosphorus, potassium, calcium and magnesium in CPH biochar were determined after the di-acid digestion of the CPH biochars. The phosphorus (P) was estimated by vanado-molybdate yellow colour method using a UV–visible spectrophotometer (UV-1601, Shimadzu, Tokyo, Japan) (Chapman and Pratt 1961). The potassium (K) content in the CPH biochar was estimated by flame photometer (model CL-378, Elico Ltd., India). The calcium and magnesium present in the CPH biochar was estimated by Versenate titration method (Cheng and Bray, 1951). The chemical properties of CPH biochar are presented in Table 2

Table 1. The chemical properties of soils under study

Parameter	Inorganic fertilizers +organics	Inorganic fertilizers alone	Unfertilized
pH	4.76	4.42	5.35
EC (µS/cm)	384.6	146.4	34.92
OC (%)	0.78	0.54	0.48
Total N (%)	0.13	0.13	0.11
Available P (ppm)	94.9	74.0	7.4
Available K (ppm)	425	449.5	27
Available Ca (ppm)	100	120	120
Available Mg (ppm)	48	48	36
Available S (ppm)	4.88	4.76	4.11
Available Fe (ppm)	37.06	24.13	17.04
Available Mn (ppm)	40.1	33.5	39.9
Available Zn (ppm)	0.77	0.63	0.53
Available Cu (ppm)	0.62	0.79	0.64

Table 2. The chemical properties of cocoa pod husk biochar

SI.No	Parameter	Value
1	pH	10.80
2	EC(mS/cm)	27.20
3	OC (%)	13.70
4	Total N (%)	1.06
5	Total P (%)	0.65
6	Total K (%)	10.30
7	Total Na (%)	5.00
8	Total Ca (%)	2.22
9	Total Mg (%)	1.32

Incubation Experiment

The phosphorus sorption was studied for soil-biochar mixtures after incubation. The CPH biochar was mixed with soil at the rate of 0, 5, 10, 20 and 40 g kg^{-1} designated as B0, B1, B2, B3 and B4, respectively. Soil alone and soil –biochar mixtures were kept at room temperature (25-30ºC) and incubated at 50% field capacity for a period of 10 days in dark conditions. The experimental design for this study was completely randomized design with five treatments and three replications. After the incubation period, the soil samples were collected and air dried for studying the phosphorus sorption. A batch adsorption study, as described by Fox and Kamprath (1970), was conducted to assess the sorption characteristics of the incubated soil and soil-biochar mixtures. The graded P levels added to the soil were 0, 20, 40, 80 and 100 mg kg^{-1} phosphorus in the form of KH_2PO_4 dissolved in 0.01 mol L^{-1} $CaCl_2$.

1. The Langmuir equation is described as

$$C/X = 1/Kb + C/b$$

Where 'X' (x/m) is the amount of sorbed P (mg kg^{-1}); 'C' is equilibrium P concentration (mg L^{-1}); 'b' is the constant related to P sorption maximum (mg kg^{-1}); and 'K' is the bonding energy (L mg^{-1}). A plot of C/(x/m) versus C gives a straight line. The constants 'K' and 'b' are obtained from the slope and intercept. For the calculation of phosphorus buffering capacity (MPBC), which is the product of phosphate affinity constant related to the binding strength and the phosphorus sorption capacity, the Langmuir constants were used.

2. The Freundlich equation is described as:

$$X = KC^{1/n}$$

Logarithm of the above equation is:

$$\log x/m = \log K + 1/n \log c$$

where 'X' is x/m, which is the phosphorus sorption (mg kg^{-1}) of soil; 'C' is the equilibrium concentration (mg L^{-1}); and 'K' and 'n' are constants in which 'n' is always greater than one. A linear plot of log x/m against log C results to the computation of 'K' and 'n' from the intercept and slope, respectively.

Phosphorus desorption

Soil samples used for phosphorus sorption studies were equilibrated with 20 mL of 0.01M calcium chloride and shaken (to and fro) for 6 h. Thereafter, the soil suspension was centrifuged and filtered. The phosphorus concentration was determined colorimetrically. The values obtained for P sorption was fitted to the following equation;

$$De/S = 1/Kd\,Dm + De/Dm$$

Where, 'S' is the amount of phosphorus adsorbed (μg g^{-1}), 'De' is the amount of phosphorus desorbed (μg mL^{-1}), 'Dm' is desorption maxima (μg g^{-1} soil) and 'Kd' is a constant related to the mobility of P in the soil.

Statistical Analysis

The data were statistically analyzed using analysis of variance (ANOVA) technique. One-way analysis of variance was employed for the least significance difference (LSD) at $p < 0.05$ level of probability to test the significance of treatment means.

Results and Discussion

Phosphorus availability in soil

The initial concentration of available phosphorus in fertilized soils (both treatments) was high and the increasing rate of CPH biochar addition further increased the concentration of available phosphorus in these soils. But in the case of control soil, the initial available phosphorus concentration was very low (7.4 ppm) and the addition of CPH biochar increased the available phosphorus gradually with the addition of CPH biochar. But at the highest rate of CPH biochar, the available phosphorus increased many fold (Fig 1). The inorganic fertilizer treatment and the inorganic + organic fertilizer treatment showed a similar trend when low doses of biochar were applied. But when the dose of biochar increased more than 10 g kg^{-1}, the inorganic treatment took an upper hand and showed higher level of available phosphorus than the inorganic + organic treatment. But these improvements in available P concentrations in fertilized soils were only 1.5-1.7 times higher than the initial P concentration. At the same time, the unfertilized soils showed gradual increase in available P concentration upon addition of CPH biochar and it reached more than 10 times at the highest rate of addition of CPH biochar (Fig 1). The lower dose of applications did not result in significantly high available phosphorus in fertilized soils. But it was very clear that addition of more than 10 g kg^{-1} CPH biochar (B2), the available phosphorus showed good improvement in all the soils. This finding is in conformity with the findings of Glaser and Lehr (2019) and Phares *et al*. (2020).

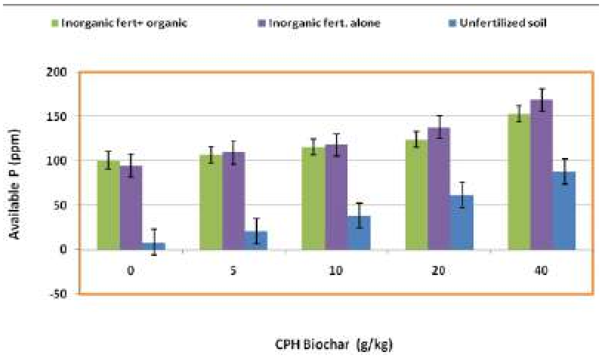


Fig. 1. Available phosphorus with CPH Biochar addition

Phosphorus Activation Coefficient (PAC)

Phosphorus activation coefficient is the ratio of available phosphorus to total phosphorus and it decides the degree of difficulty of converting total phosphorus to available phosphorus. Hence, the phosphorus activation coefficient is very important factor in predicting the fertility of soil; higher the coefficient, the more available is phosphorus in soil for promoting plant growth (Wu *et al*., 2017). Here, it is clear that in the absence of CPH biochar, the unfertilized soil, which is deficient in available P, showed the lowest phosphorus activation coefficient than the fertilized soils. But upon the addition of CPH biochar, the phosphorus activation coefficient significantly increased in unfertilized soil in the order from B1 to B4. However, the addition of CPH biochar up to B2 did not show significant difference in PAC of fertilized soils, where high available phosphorus was present. As the amount of biochar addition increased to more than 10 g kg^{-1}, the PAC showed significant improvement in fertilized soils.

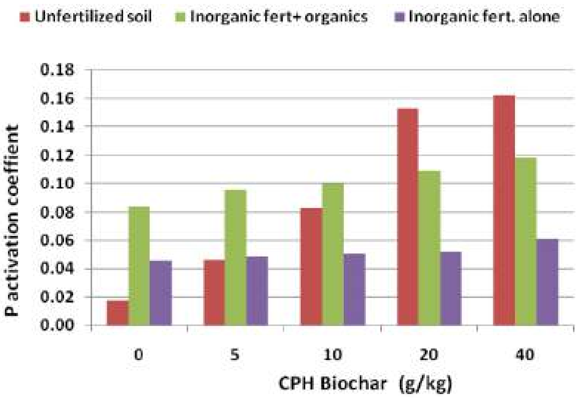


Fig. 2. Phosphorus Activation coefficient with CPH Biochar addition

Phosphorus sorption study

The phosphorus sorption data of soil samples of all three treatments, with different doses of CPH biochar, can be described by using Langmuir equation ® >0.98, P<0.01). From Fig 3, it was clear that the phosphorus sorption increased by increasing the initial phosphorus concentration in all the soil samples irrespective of the biochar addition. Since phosphorus adsorption in soil is a multi stage kinetic process, the initial adsorption is chemical in nature and hence, it is fast and later it may slow down (Wang and Liang, 2014). After addition of phosphorus in all three categories of soils, lowest phosphorus sorption was observed in the one without biochar. Also, in lower levels of CPH biochar addition, all three treatment soils behaved similar to that of soil without biochar in all the concentrations of phosphorus. As the added phosphorus concentration was less than 20 mg L^{-1}, there was no significant change in the phosphorus sorption with the addition of 0-10 g kg^{-1} biochar. But when the phosphorus concentration was increased, the P sorption increased in soils with more than 10 g kg^{-1} CPH biochar. This indicates that the effect of CPH biochar on phosphorus sorption is more obvious at higher rate of CPH biochar and higher levels of phosphorus addition (Xu *et al.*, 2014; Rashmi *et al.*, 2019).

In unfertilized soils, the lowest sorption value was recorded by soil without biochar at the highest concentration of phosphorus addition (347 mg kg^{-1}) compared to soil with biochar. The addition of CPH biochar at the rate of 5 g kg^{-1} had no effect on the phosphorus sorption at any concentration of phosphorus addition and behaved similar to that of the soil without biochar. But the phosphorus sorption slowly increased with the addition of biochar at the rate of 10 g kg^{-1}, though it was not significant. However, when the concentration of biochar increased at the rate of 20 g kg^{-1}, a significant increase in phosphorus sorption was observed from lower levels of phosphorus addition up to a concentration of 539 mg kg^{-1}. At the highest rate of biochar addition (40 g kg^{-1}), the phosphorus sorption showed a significantly high phosphorus adsorption in all the concentrations of added phosphorus. The highest sorption value recorded in this rate was 805 mg kg^{-1}. CPH biochar at higher rate might alter the pH of the soil by releasing more potassium, sodium, calcium and magnesium to soil solution and thus increase the sorption capacity of the soil (Jha *et al.*, 2016).

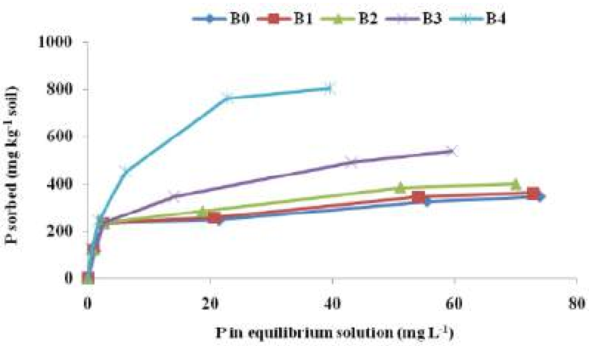


Fig. 3. Phosphorus sorption isotherms for unfertilized soil

Soils fertilized with inorganics alone was having the highest initial available phosphorus content (Table 1). Compared to the soil fertilized with inorganics + organics, the soil with inorganic fertilizer alone also showed a slightly less rapid increase in chemisorptions of phosphorus initially upon addition of phosphorus especially due to the high available phosphorus in soil. In later stages, as the available adsorption sites were reduced, the rate of increase of phosphorus sorption again became slow. But due to the addition of CPH biochar, the added adsorption sites became available and slowly the adsorption value became high and the highest value was recorded by the highest CPH biochar treatment (B4). At lower doses of CPH biochar, the phosphorus sorption was not significantly high compared to the soil without biochar as observed in unfertilized soils. Here, the biochar alone played a role in increasing the adsorption sites and increased the phosphorus adsorption up to 935 mg kg^{-1} in the highest rate of CPH biochar (40 g kg^{-1}). Significantly high phosphorus adsorption was noticed at CPH biochar @ 10 g kg^{-1} onwards and this trend was not noticed in unfertilized soil and soil fertilized with inorganics + organics. Initial pH of the soil also might influence the phosphorus adsorption as the lowest pH (4.42) was recorded in the soil fertilized with inorganics alone.

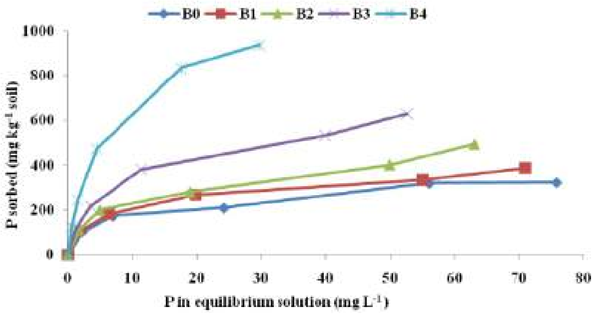


Fig. 4. Phosphorus sorption isotherms for soils fertilized with inorganics alone

In the case of soils fertilized with inorganics + organics, the phosphorus sorption showed a similar trend as in the case of unfertilized soil. Here also, the lowest phosphorus sorption was recorded by the soil without biochar at the highest concentration of P addition (343 mg kg^{-1}) which was slightly lower than the unfertilized soil. As the CPH biochar concentration increased, the phosphorus sorption was found to increase in the biochar-added soils, albeit slowly, at all the concentrations of added phosphorus, up to 10 g kg^{-1}. Similar to unfertilized soils, here also significantly high phosphorus sorption was recorded when the rate of CPH biochar was more than 10 g kg^{-1}. At initial addition of phosphorus, the phosphorus adsorption showed a fast increase; thereafter, the rate of adsorption became slow. This might be due to the chemical adsorption process which might slow down later due to the saturation of phosphorus adsorption sites by the addition of high amount of phosphorus (Yang *et al*., 2019). The highest rate of CPH biochar showed the highest value of P adsorption (995 mg kg^{-1}) at the highest concentration of phosphorus in the equilibrium solution. CPH biochar addition might have increased the phosphorus adsorption sites, thereby, increasing the phosphorus adsorption in soil-biochar mixtures. It was very clear that there is a direct relationship between quantity of CPH biochar and the phosphorus adsorption. In soils fertilized with inorganics + organics, the initial increase in phosphorus sorption was not as sharp as in the unfertilized soils. This might be due to the lower available adsorption sites due to the presence of high available phosphorus in these soils. Along with biochar, the presence of organic manures in this soil also influenced the adsorption sites and increased the phosphorus adsorption ultimately.

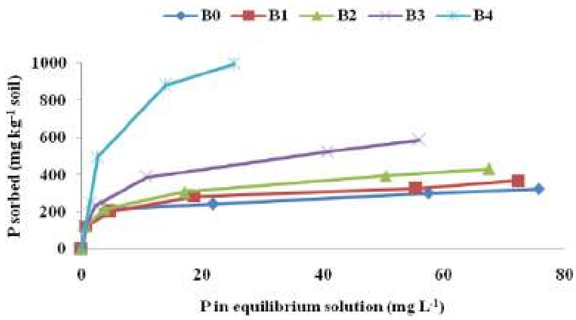
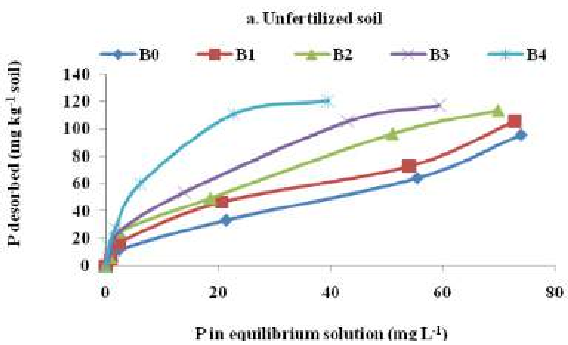
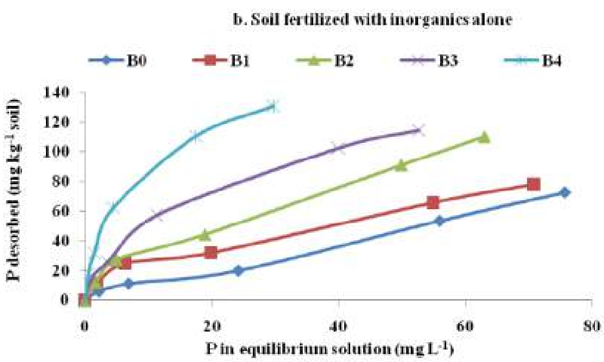


Fig. 5. Phosphorus sorption isotherms for soils fertilized with inorganics + organics

Phosphorus desorption study

Desorption of phosphorus is an important process in phosphorus cycle as the desorbed phosphorus will determine the availability of phosphorus for reuse (Wang and Liang, 2014). The desorbed phosphorus will be always less than the adsorbed phosphorus because of the irreversibility of the adsorption process. From Fig 6, it was clear that as the phosphorus addition increased, the desorption of phosphorus also increased, irrespective of the CPH biochar addition. Also, the phosphorus desorption was low at lower levels of P addition and increased with the solution phosphorus. During the initial chemical adsorption process, the phosphorus binding sites were filled rapidly and as the phosphorus concentration increased, the binding sites got saturated with phosphorus. In the later physical adsorption stage, the excess phosphorus present got desorbed. The addition of CPH biochar influenced the adsorption sites and hence, more adsorption could be seen in the soil with high CPH biochar. The desorption was also found to increase with the addition of biochar and this could increase the availability of phosphorus in the soil. The rate as well as amount of phosphorus addition recorded higher phosphorus desorption across all soils. Similar finding was reported by Yang *et al*. (2019) with organic matter addition. As the rate of CPH biochar increased to more than 10 g kg^{-1}, desorption also increased in all the soils. Similar to adsorption, highest desorption was also observed at the highest rate (40 g kg^{-1}) of biochar addition in all the soils. The lowest desorption at different rates of biochar addition was found in unfertilized soil than the fertilized soils. The highest value of desorption was recorded by the soil fertilized with inorganics + organics. But in the unfertilized soil also, the addition of biochar at higher rate (@10 g kg^{-1}) could improve the phosphorus desorption.





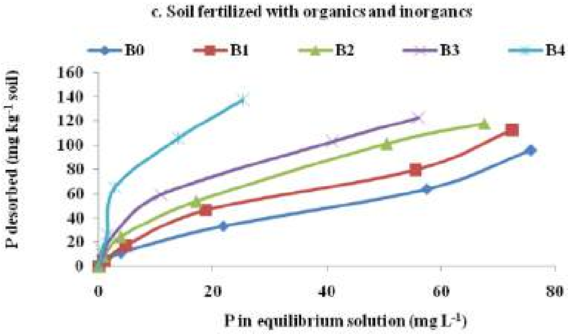


Fig. 6. Phosphorus desorption in different soils

Conclusion

From this study, it was concluded that the addition of Cocoa Pod Husk (CPH) biochar increased the phosphorus adsorption and desorption in low pH soil. Both the processes are having equal importance as far as phosphorus availability is considered. The rate of biochar also played a good role in both these processes. A higher rate (>10 g kg^{-1}) of CPH biochar during desorption process could make the adsorbed phosphorus more available. At lower levels of phosphorus in soil, the biochar addition could improve the phosphorus availability and hence, it can be recommended as an amendment in low pH soils, particularly in organic farming practices.

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